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Swollen-state polymerization of poly(ethylene terephthalate): kinetic analysis of reaction rate and polymerization conditions

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Ultra-high-molecular-weight poly(ethylene terephthalate) (UHMW-PET) with an intrinsic viscosity exceeding 2 dl g^{-1} ($M_n \approx 1.1 \times 10^5$) was obtained by swollen-state polymerization with hydrogenated terphenyl as the solvent. The rate of swollen-state polymerization was described well by Tomita's kinetics for a melt-phase polycondensation reaction. This suggested that there was no essential difference in the kinetics between swollen-state polymerization and conventional melt-phase polymerization. The activation energy of swollen-state polymerization obtained was 21 kcal mol^{-1}, similar to that of conventional melt-phase polymerization (23 kcal mol^{-1}). Other polymerization conditions, that is, the particle size of the starting PET, the flow rate of inert gas and the ratio of solvent to PET, are related to the rate of swollen-state polymerization. Compared with the rate constants of conventional polymerization methods such as melt-phase polymerization and solid-state polymerization, the propagation rate of swollen-state polymerization was about three to five times faster than that of solid-state polymerization at 220°C, whereas the rate constant of the degradation reaction in the swollen state was of the same order as that in the solid state. These rate effects have resulted in UHMW-PET.

(Keywords: poly(ethylene terephthalate); ultra-high molecular weight; swollen state)

INTRODUCTION

Poly(ethylene terephthalate) (PET) is used as fibres, films, bottles for beverages and plastics. Many experimental studies on the polymerization of PET to obtain an ultra-high molecular weight have been devoted to melt-phase polymerization and solid-state polymerization. For high tenacity and high modulus fibres using PET, some authors have claimed the importance of high molecular weight[1,2].

Ultra-high-molecular-weight PET (UHMW-PET) with an intrinsic viscosity (*IV*) of 2.3 dl g^{-1} was obtained from melt-phase polymerization with the addition of long-chain aliphatic acid with glycol[3]. From thin-film polymerization, UHMW-PET with $IV \geqslant 2$ dl g^{-1} was disclosed in a patent[4].

Also, UHMW-PET having $IV \approx 2$ dl g^{-1} was obtained by special solid-state polymerization by Hsu[5,6]. Cohn reported that solid-state polymerization using a porous and fibrous structure of PET prepolymer obtained by precipitating from a PET solution induced UHMW-PET with high molecular weight, $IV = 2$–5 dl g^{-1} ($M_n = 1.1 \sim 4.2 \times 10^5$)[7,8]. However, it is difficult to obtain such UHMW-PET by conventional melt-phase or solid-state polymerization.

In a previous article[9], we reported a new polymerization technique to obtain UHMW-PET, i.e. swollen-state polymerization in specific solvent, and discussed the effects of solvents and the swollen-state temperature. When a hydrogenated terphenyl was used as the solvent, UHMW-PET with $IV = 2$–3 dl g^{-1} was obtained and a honeycomb-like structure was observed in the UHMW-PET particles.

In this paper, we extend the study of swollen-state polymerization kinetics and conditions to understand the polymerization mechanism.

EXPERIMENTAL

The details of the experimental methods were described in a previous paper[9]. A mixture of PET and hydrogenated terphenyl as the solvent was used in this study. Initial prepolymer chips (molecular weight of PET, $IV = 0.6$ dl g^{-1}) were obtained from conventional melt-phase polymerization catalysed by antimony trioxide, 0.05 mol% (to acid component). The standard conditions of swollen-state polymerization were as follows. The prepolymer PET was granulated to 3.2 mm average diameter. A mixture of solvent and PET (solvent ratio, $SR = 5.3$ litres solvent kg^{-1} PET) was pretreated with stirring overnight ($\sim$16 h) at 210°C under nitrogen atmosphere. After pretreatment, the PET prepolymer polymerized to $IV = 0.9$–1.0 dl g^{-1}. Then the temperature of the mixture was raised to 237°C with bubbling nitrogen (N_2: 67 l h^{-1} kg^{-1} PET).

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The *IV* of the polymer was measured in the same manner as in the previous study. The number-average molecular weight (M_n) of UHMW-PET was calculated by[10]:

$$IV = 7.5 \times 10^{-4} (M_n)^{0.68} \qquad (1)$$

The molecular weight distribution of PET obtained was estimated by size-exclusion chromatography using a mixture of chlorobenzene/*m*-cresol (1/3 (vol/vol)) as the eluent with standard polystyrene calibration.

RESULTS AND DISCUSSION

A desirable solvent for swollen-state polymerization of PET needs to swell but not to dissolve the PET at polymerization temperature. Furthermore, the solvents for the polymerization must possess thermal stability at the polymerization temperature, i.e. high boiling and high decomposition temperature. In a previous paper[9], it was found that solvents having a similar solubility parameter to PET were desirable for attaining a higher molecular weight at the same polymerization temperature. The rate of swollen-state polymerization was strongly related to the degree of swell, i.e. the amount of impregnated solvent in swollen PET. When a hydrogenated terphenyl was used as the solvent, UHMW-PET having $IV = 2\text{–}3\ \text{dl g}^{-1}$ ($M_n \geqslant 1.1 \times 10^5$) was obtained.

Kinetic analysis

The propagation and degradation reactions were confirmed in the melt-phase polycondensation of bis(2-hydroxyethyl) terephthalate (BHET) by Tomita[11]. According to Tomita's kinetics of the polycondensation of BHET, the rate of polycondensation is given by:

$$n = \frac{1}{1 + K_p t} + \frac{2}{3} K_d t \qquad (2)$$

where n is the mole number of the polymer, K_p is a rate parameter for the propagation reaction, K_d is that for the degradation reaction and t is the reaction time. The value of M_n at any given time was calculated using equation (3), where M_{n0} means the initial molecular weight of prepolymer after pretreatment:

$$M_n = \frac{192}{n} + M_{n0} \qquad (3)$$

Figure 1 shows the time variation of M_n at various swollen-state temperatures. The value of M_n increases with reaction time and swollen-state polymerization temperature. Note that the initial M_n is calculated from *IV* after pretreatment at 210°C for 16 h (overnight).

The values of K_p and K_d are calculated by least-squares fits of the obtained data. The results are shown by the solid line in *Figure 1*. One sees that all plots are nicely located on the calculated curves and the maximum M_n is well interpreted. It is interesting to note that the same kinetics are applicable to the swollen-state polymerization.

Figure 2 shows the Arrhenius plot for the values K_p and K_d. The linear relation is seen in both the K_p and K_d plots, indicating that an apparent activation energy can be estimated from the slope. The apparent activation energy for propagation, E_p, is 21 kcal mol^{-1} and for degradation, E_d, is 40 kcal mol^{-1}, respectively.

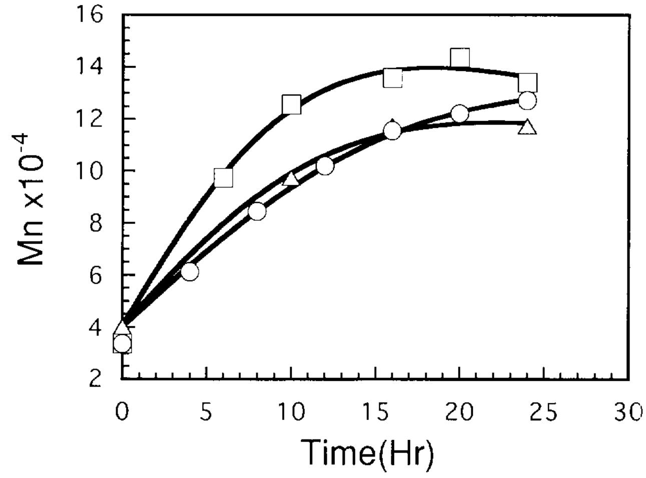

Figure 1 Molecular weight as a function of reaction time at various swollen-state temperatures: (△) 232°C; (○) 237°C; (□) 242°C

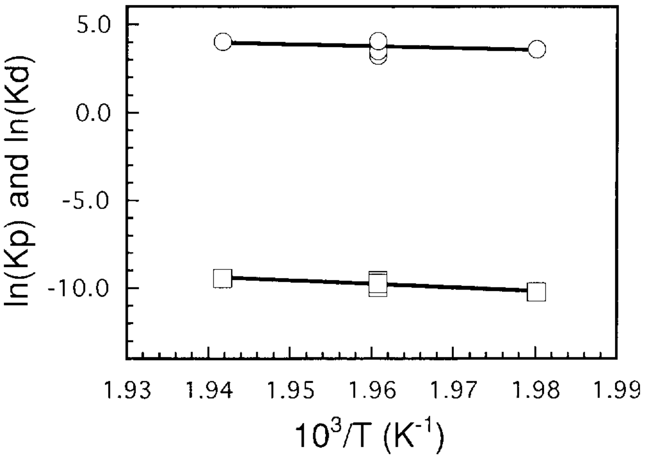

Figure 2 Arrhenius plot of the rate constant at various swollen-state temperatures: (○) K_p; (□) K_d

That is, swollen-state polymerization has the same temperature sensitivity as melt-phase polymerization ($E_p = 23.7$ kcal mol^{-1}, $E_d = 46.6$ kcal mol^{-1})[12]. These results imply that there is no essential difference in the kinetics between swollen-state polymerization and melt-phase polymerization.

Effect of initial particle size

In conventional solid-state polymerization, the by-product glycol is eliminated from the surface of the PET particle so that the reaction rate is dependent on the particle size. In swollen-state polymerization, however, the effect of the particle size may be smaller due to the enhanced mobility of the polymer chain. To confirm this point, the influence of particle size on swollen-state polymerization was examined.

Figure 3 shows the effect of the initial particle size of PET on swollen-state polymerization. It should be noted that the solid lines in *Figures 3*, *5*, *6* and *7* express the results calculated by equation (2). One can see no difference of the polymerization rate between 0.2 and 1.8 mm in diameter, but at 3.2 mm a somewhat slower polymerization rate is seen. It is found that an initial size below 1.8 mm diameter is sufficient to impregnate the

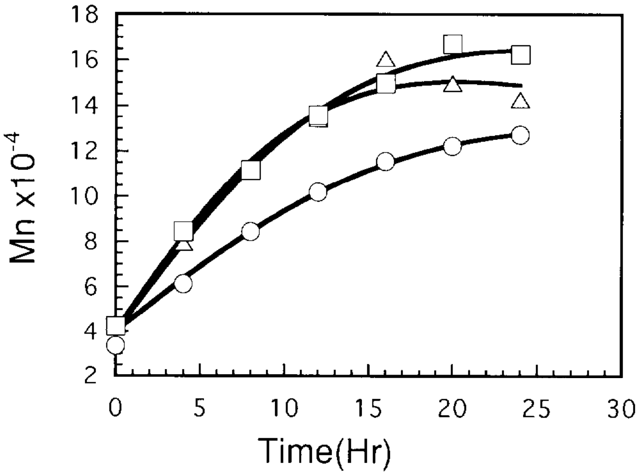

Figure 3 Effect of particle size: (○) 3.2 mm; (□) 1.8 mm; (△) 0.2 mm. Temperature 237°C, N_2 67 l h^{-1} kg^{-1}; *SR* 5.3 l kg^{-1}

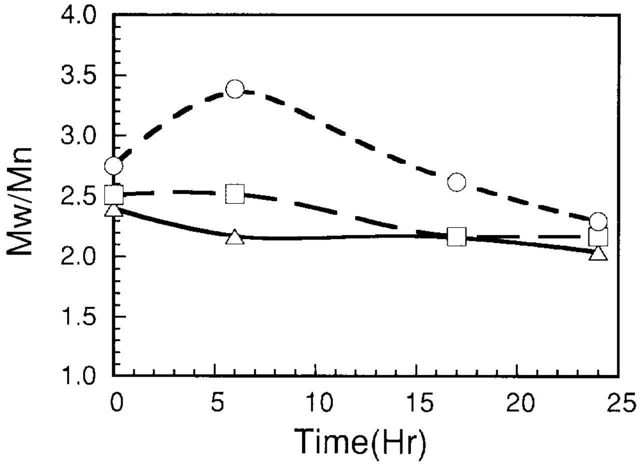

Figure 4 Molecular weight distribution as a function of reaction time. Particle size: (○) 3.2 mm; (□) 1.8 mm; (△) 0.2 mm. Temperature 237°C, N_2 67 l h^{-1} kg^{-1}; *SR* 5.3 l kg^{-1}

solvent. The same trend is observed in the time variation of molecular weight distribution. *Figure 4* shows the change of M_w (weight-average molecular weight)/M_n by size exclusion chromatography (s.e.c.) with reaction time at 237°C. Also, the values of M_w/M_n for swollen-state polymerization for different particle sizes are close to the statistical values[13] at the late stage (>20 h).

Effect of flow rate of nitrogen gas and solvent/PET ratio

The by-product glycol from the PET particle is extracted by the solvent and evaporated from the solvent by nitrogen bubbling. The rate of nitrogen flow may be a significant polymerization condition.

Figure 5 shows the influence of flow rate on the polymerization rate at 237°C. An accelerated behaviour of reaction rate is observed with flow rate, suggesting that at the high flow rate the glycol is eliminated from the solvent and therefore the value of K_p becomes larger than at the low flow rate. Also the solvent/PET ratio (*SR*) influences the reaction rate, as shown in *Figure 6*. These results imply that the amount of solvent is related to the concentration of glycol in the solvent so that there is a difference between the two solvent/PET ratios.

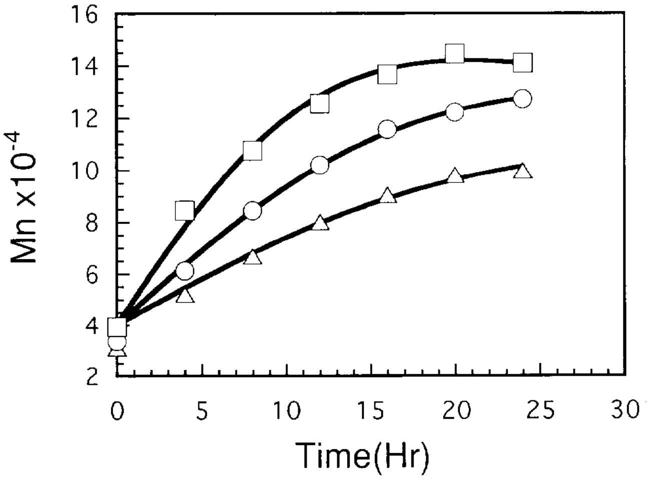

Figure 5 Effect of N_2 flow rate on swollen-state polymerization: (△) 34; (○) 67; (□) 134 l h^{-1} kg^{-1}. Temperature 237°C; particle size 3.2 mm; solvent ratio 5.3 l kg^{-1}

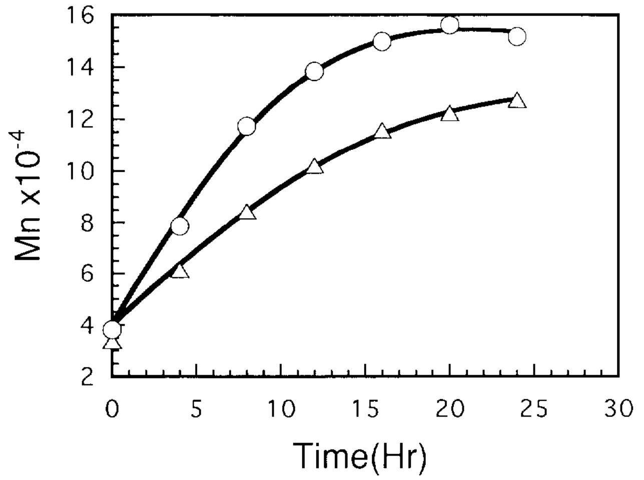

Figure 6 Effect of ratio of solvent to PET (*SR*). (○) *SR* = 5.3; (□) *SR* = 10 l kg^{-1}. Temperature 237°C; N_2 67 l h^{-1} kg^{-1}; particle size 3.2 mm

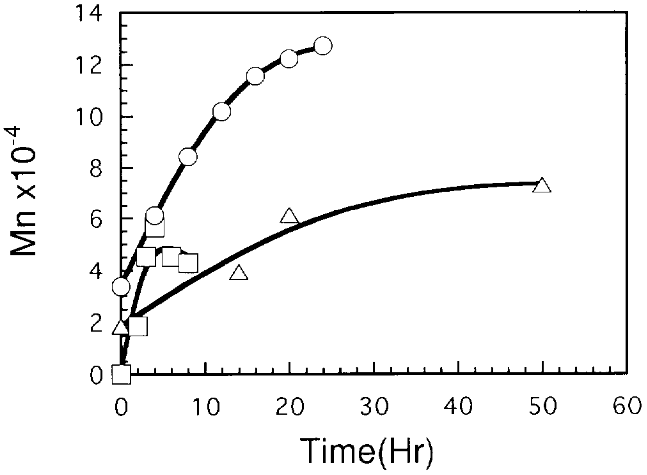

Figure 7 Comparison of the rate of swollen-state polymerization with that of conventional polymerization: (□) melt-phase polymerization; (△) solid-state polymerization; (○) swollen-state polymerization

Table 1 Rate constants obtained by kinetic analysis

	K_p (l mol^{-1} h^{-1})	K_d($\times 10^5$) (mol h^{-1})
Solid-state polymerization (220°C)	10.92	5.000
Swollen-state polymerization (237°C)	35.50	5.577
Swollen-state polymerization (242°C)	55.85	7.864
Melt-phase polymerization (280°C)	91.07	53.78

However, at present we cannot discuss quantitatively the influence of the by-product glycol on the kinetic parameters.

Comparison of the rate constants

In order to compare the rate constants, conventional melt-phase and solid-state polymerization were carried out with the same catalyst concentration and the same chip size. *Figure 7* shows the molecular weight change as a function of polymerization time. The temperature of melt-phase and solid-state polymerization was 275 and 220°C, respectively. It is to be emphasized that the rate of melt-phase and solid-state polymerization is strongly influenced by the polymerization apparatus and conditions. Each plot within the framework is nicely located on the calculated curves, expressed as the solid line in *Figure 7*. The equations well interpreted the relationship between propagation and degradation. K_p and K_d values calculated from the equation are listed in *Table 1*. The propagation rate in the swollen state was about three to five times faster than that in the solid state at 220°C, whereas the rate constant of the degradation reaction in the swollen state was of the same order as in the solid state. These rate effects have resulted in UHMW-PET.

CONCLUSION

On the basis of the kinetic analysis, the kinetics of the melt-phase polycondensation reaction was found to be valid for the swollen-state polymerization. The propagation reaction with large K_p proceeded and the degradation reaction with small K_d was negligibly small at the polymerization temperature. The size of prepolymer, the nitrogen flow rate and the solvent/PET ratio were related to the rate of polymerization.

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